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Electrolytically Formed Coating for Magnesium Alloys

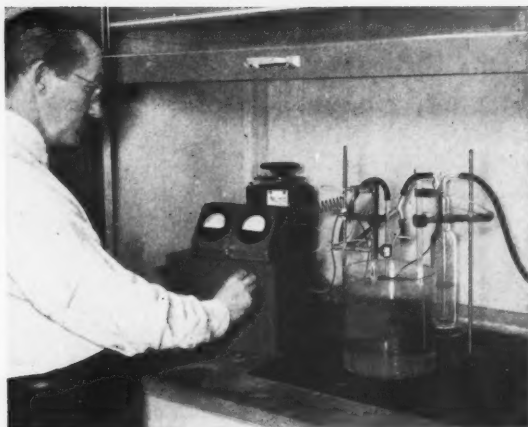
A LOW-VOLTAGE alkaline chromate process for depositing protective coatings on magnesium alloys has been investigated by H. A. Salmon, M. J. Kronenberg, and F. Ogburn of the National Bureau of Standards electrodeposition laboratories, under the sponsorship of the Department of the Army. Coatings produced by this method provide protection against salt-spray corrosion equivalent to that of coatings obtained from other anodizing processes currently used. The NBS process is potentially more economical than the other methods, however, because it uses a low-voltage power supply and only two chemical constituents other than water.

Lightweight, easily machined metals are in increasing demand by industry, and magnesium is one of the most important to become available in commercial quantities in recent years. The use of magnesium and its alloys is limited, however, by its low resistance to corrosion—salt-spray corrosion, in particular. Protective coatings obtained from the Bureau's simple alkaline chromate process should lead to wider utilization of magnesium alloys for lightweight equipment and for many aircraft and shipboard components where corrosive atmospheres prevent use of the uncoated metal.

The NBS process is similar to electroplating except that alternating current is used instead of direct current,

and the coating is formed on both electrodes. Some material is deposited out of the solution onto the electrodes in the anodizing process, but the coating is mainly material formed by the chemical reaction between the metallic electrode and the components of the electrolyte. The NBS method for coating magnesium alloys differs from the acid chromate and the HAE anodizing processes in two respects: (1) It operates at a much lower voltage—usually 10 to 12 v ac, and (2) the electrolytic bath contains only two constituents other than water—sodium or potassium hydroxide and the corresponding chromate. In the NBS process, a current of 80 to 140 amp/ft² is passed through the bath 20 to 40 min, at a temperature of 150 to 170° F. Under these conditions, a coating 1 to 2 mils thick will form on the magnesium alloy electrodes.

The coating is smooth and gray-green in color, but not as uniform in appearance as either the HAE or the acid chromate coatings. The surface exhibits some sheen if the initial surface is very smooth. Gas adsorption measurements (Brunauer-Emmett-Teller method) reveal that the coating has a smaller effective surface area than HAE coatings. If anodized panels are bent or flexed, then the coatings crack on the tension side of the bend and chip or shatter on the compression side.



Laboratory equipment for electrodepositing protective coatings on magnesium alloys. This alkaline chromate process is simpler than other anodizing processes in that it uses a low-voltage power supply and only two chemical constituents other than water—sodium or potassium hydroxide and the corresponding chromate.

While the coating distribution is not as uniform as those produced by processes requiring higher voltages, such as the HAE process, it is more even when suitable racking procedures are used. Complete coverage can then be obtained over a limited range of temperature for a given current density. For example, if the process is operated at 80 amp/ft², a temperature of 60° C is required to obtain complete coverage of specimen panels. At lower temperatures, the panels remain bare near the edges. At higher current densities, the minimum temperature required for complete coverage is higher. However, indications are that temperatures above 75° C yield coatings having poorer corrosion protection.

The work at the Bureau shows the outstanding characteristic of coatings produced in these alkaline chromate baths to be resistance to salt-spray corrosion. Corrosion resistance of coatings from many baths of various compositions, including the HAE and the acid chromate, were compared with those of coatings produced from this newly developed bath. When the test specimens were exposed to salt spray in equipment operated according to Federal Specification QQ-M151 for 12 days, the coatings applied by the alkaline chromate bath appeared to be the most resistant.

The salt-spray protective value of the coating is controlled by the current density and bath temperature. Variations in current between 80 and 140 amp/ft² have little effect on the corrosion resistance, but lower current densities yield coatings of inferior protective value. Increasing the temperature above that required for complete coverage also tends to reduce the protection against salt spray. Direct current has been used in this process to produce uniform coatings on panels in solutions of appropriate composition. The

TABLE 1. Relation of alkali concentration of bath to salt-spray resistance of coatings deposited from a bath containing 1.0 M chromate

NaOH concentration	Coating thickness	Corrosion spots (28 days exposure)
<i>Molar</i>	<i>Mils</i>	
0	Unsatisfactory	—
0.1	1.6	55
.2	1.7	41
.3	1.7	36
.5	1.7	43

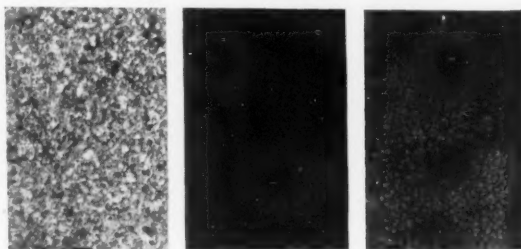
TABLE 2. Relation of chromate concentration of bath to salt-spray resistance of coatings deposited from a bath containing 0.3 M alkali

K ₂ CrO ₄ concentration	Coating time	Corrosion spots (4 days exposure)
<i>Molar</i>	<i>Minutes</i>	
0	20	100
0.1	20	14
.2	20	13
.3	20	13
.4	20	6
.8	20	6
1.2	20	5
1.6	20	5

TABLE 3. Analyses of coatings from alkaline chromate baths

Coating	Thickness	Chromate concentration in bath	Cr ⁶⁺	Total			Loss on ignition over bunsen flame
				Cr	Mg	CO ₂	
	<i>Mils</i>	<i>Molar</i>	<i>%</i>	<i>%</i>	<i>%</i>	<i>%</i>	<i>%</i>
1	1.8	0.1	0.26	0.68	36.7	4.4	37.6
2	1.4	.5	.52	1.05	36.2	4.6	38.4
3	1.2	1.0	.72	1.36	36.1	4.8	37.1
4	1.4	1.5	1.00	1.78	36.1	3.9	35.8

Magnesium alloy samples used to test corrosion resistance of alkaline chromate coatings. Sample at left is uncoated, and has been exposed to salt spray. Panel in center has been coated by alkaline chromate process. Specimen at right has been coated similarly to center panel, but has been exposed to salt spray as well. Comparison of coated and uncoated magnesium alloy samples indicate the measure of corrosion resistance to salt spray provided by the NBS alkaline chromate process.



salt-spray tests indicated that these coated panels were somewhat inferior to those coated in the preferred a-bath.

As part of the investigation, several organic coatings—such as lacquers or paints—were tested for adhesion to the chromate coating. The adhesion was satisfactory if the specimens were not subjected to bending or flexing. When the panels are bent, loss of adhesion occurs on coatings 0.5 mil or more in thickness because

of the failure of the electrodeposited coating. However, the adhesion is satisfactory on thinner coatings.

For further technical details, see Electrolytic coatings on magnesium base alloys from alkaline chromate solutions, by F. Ogburn, H. I. Salmon, M. L. Kronenberg, Plating 42, 271 (March 1955). This work is a detailed investigation of a process generally described in U. S. Patent 2,314,341, granted to Robert W. Buzzard, March 23, 1943.

Automatic Potting Machine

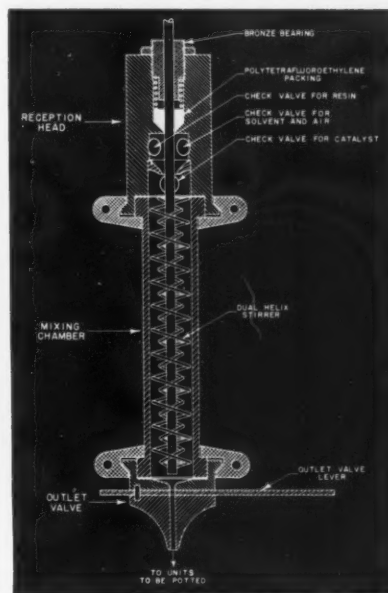
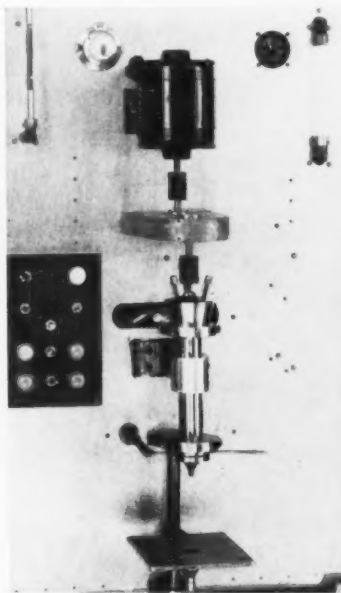
AN AUTOMATIC MACHINE for potting electronic components has been developed by J. E. Sensi and P. J. Franklin of the Bureau.¹ The machine feeds a casting resin and a catalyst from heated tanks through proportioning pumps into a mixing chamber. After the liquids are thoroughly stirred, they are permitted to flow into the electronic assembly. Since the series of operations is continuous, resin can be mixed as needed, and the pot-life requirements of the resin-catalyst mixture are reduced to a minimum. Although

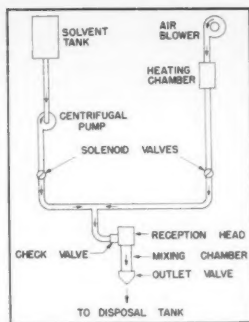
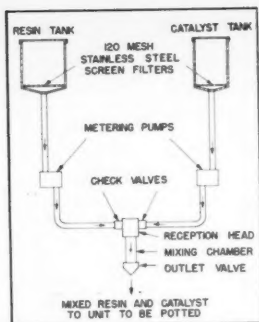
the machine was originally designed for laboratory use, it has been found advantageous in production-line applications.

A rapidly growing use for casting resins is in the potting of electronic components and subassemblies which must be capable of enduring extreme environmental and handling conditions. Such units are potted to protect them against moisture, heat, pressure, shock, and vibration, arcing between components, and long periods of storage under adverse conditions. Casting resins, which are simply a catalyst and a resin mixed in correct proportions, are now being used extensively to meet these conditions. However, the pouring life or pot life of certain of these mixtures is very short, sometimes only a few minutes. This short pot life requires small batch mixing operations that are wasteful in both time and materials. The development of an automatic mixing machine has overcome this difficulty.

¹The automatic potting machine was developed under the NBS ordnance development program, which has since been transferred to the Department of Defense and is known as the Diamond Ordnance Fuze Laboratory. Since this machine was designed, two others have appeared on the market. One is described in *Plastics World* 12, 9, 7 (1954). The other has been announced by Applied Engineering Associates, 1952 Flushing Avenue, Brooklyn 37, N. Y.

Automatic potting machine developed at NBS for mixing casting resin with a catalyst and pouring the mixture into electronic components. Since the operation is continuous, the pot-life requirements of the resin-catalyst are reduced to a minimum. Control panel and mixing chamber are illustrated. Right: A schematic of mixing chamber showing the dual-helix stirrer which is motor driven at appropriate speed for mixing.





Left: Flow diagram of resin-catalyst mixing system. Resin and catalyst are pumped in desired proportions by metering pumps through check valves and into reception head of mixing chamber. Resin and catalyst are mixed continuously, with only a small volume of material in the mixing chamber at any given time. **Right:** Flow diagram of solvent flushing system. When potting machine stands idle for a period of time longer than the pot-life of the resin-catalyst mixture, mixing chamber is purged of the compound and then thoroughly flushed with solvent and then drained. The chamber is dried with warm air to remove all solvent traces. Machine is then ready for operation again without solvent present to inhibit polymerization of new batch of resin-catalyst mixture.

The potting machine is composed of three independent systems: A heating system, a resin-catalyst mixing system, and a purging system. The three systems are coordinated by manually operated switches.

The heating system maintains the resin and catalyst at elevated temperatures in order to reduce viscosity and to speed leveling in the potted unit. A centrifugal pump circulates water through a tank containing an immersion-type heater and through coils in the resin and catalyst storage tanks. Liquids with higher boiling points may be substituted for water where required by a particular resin.

The resin and catalyst, heated by the circulating water, flow from the reservoir tanks through 120-mesh screens to the suction sides of two proportioning gear pumps whose volume output is controlled by the speed of the metering gears. The pumps are driven by a single motor through a gear train at the speeds required to give the desired volumetric ratio of resin to catalyst. The liquids flow from the pumps to spring-loaded check valves in the reception head of a mixer. The valves are opened by the pressure imparted by the pumps to the liquids, which then enter the mixing chamber.

The mixing chamber is a small tube having a large length-to-diameter ratio and containing a dual-helix stirrer. The outer portion of the stirrer is a right-hand helix, and the inner portion is a left-hand helix. The assembly is driven by a small motor. A gear reduction box between the motor and mixing chamber provides the desired stirrer speed. The stirrer shaft is enclosed in a bronze bearing with polytetrafluoroethylene packing. The machine continuously mixes resin and catalyst as they are required, with only a small volume of the liquid in the mixing chamber at any given time. Continuous operation alleviates the problem of working with premixed batches which have very short pot lives, since the mixture does not have sufficient time to harden before being used.

A purging system is built into the machine to clean thoroughly all areas with which the mixed resin and catalyst have been in contact. It is used whenever the machine must stand idle longer than the pot life of the mixture. Purging consists of two operations: Flushing solvent through the mixing chamber and blowing warm air through the chamber to evaporate the remaining solvent.

A solvent for the resin mixture is stored in a small

tank mounted on the machine. A small centrifugal pump forces the solvent into the mixing chamber when the appropriate switches on the control panel are operated; at the same time the flow of resin and catalyst is stopped. The solvent flushes the resin mixture out of the chamber through the outlet valve. The amount of solvent used for a complete flushing varies, but usually not more than 3 or 4 times the volume of the mixing chamber is required.

After the chamber is purged of resin, the drying system is turned on to evaporate any remaining solvent. The system consists simply of a small centrifugal blower which forces air over a set of heating elements and into the mixing chamber. At the end of the purging cycle the machine is free of any solvents that might inhibit the polymerization of the resin, and is again ready for operation.

The machine is put into operation by first closing a master switch that controls the immersion heater. When the resin and catalyst are at the proper temperature, the stirrer switch is closed; it remains closed throughout the mixing and purging cycles. The stirrer is stopped momentarily, however, to prevent air from being stirred into the incoming mixture while the mixing chamber is first being filled. When the chamber is full, the stirrer goes back into operation. After the constituents are mixed, the machine is ready to deliver a homogeneous mixture of resin and catalyst at the desired temperature and proportions. The operation then becomes a continuous one, and the casting mixture flows through the outlet valve whenever it is opened.

The units to be potted are supported on an adjustable-height table while they are being filled. An outlet tube from the mixing chamber enters the unit to be potted at the top and extends to the bottom, and the resin, rather than flowing down on the mass of wiring and components, is allowed to fill the unit from the bottom up, thus minimizing air pockets and increasing the rate of production. The machine can easily be converted for use with multiconstituent resins by the introduction of a suitable number of tanks, valves, and metering pumps.

For further technical details, see Automatic potting machine, by John E. Sensi and Philip J. Franklin, *Elec. Mfg.* (in press).

Zone Melting Apparatus

AN AUTOMATIC laboratory-type zone melter recently constructed at the Bureau combines versatility and dependability with unusual simplicity and ease of operation. The device is now being used in the Bureau's solid state physics laboratory to obtain extremely high purity in semiconducting materials.

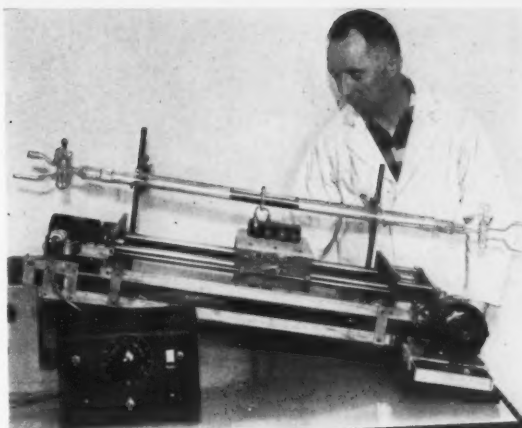
The zone melting process has been used to purify metals for several years and is now a familiar industrial and scientific tool. By this process it is possible in some cases to obtain such a high degree of purity that the remaining impurities are almost undetectable by present analytical methods. By the process it is also possible to blend in evenly a specific amount of another metal to obtain a desired alloy. Although a number of zone melting devices somewhat similar to the NBS apparatus are in operation in other laboratories, none of these have been fully described in the literature.

In the NBS zone melter, the solid material to be purified is placed in a fused silica or carbon boat within a vycor tube. A water-cooled induction coil, concentric with the vycor tube, is then made to pass slowly along the length of the solid material. The resultant heating effect produces a small molten zone in the bar of material. This molten zone moves along the length of the bar with the coil, causing a continuous separation of impurities at the zone boundaries. The separation occurs in such a manner that after the material has been melted a number of times, the impurities tend to concentrate at one end of the bar. The apparatus is designed so that the operation can be carried out either in a vacuum or in an inert atmosphere.

The heater coil, powered by a commercial 5-kw unit, is mounted on a three-wheeled carriage which provides a useful travel of 18 in. The wheels, ball-bearing mounted, engage and are guided by two $\frac{3}{4}$ -in. diam rods or tracks. The motion is supplied to the carriage by a $\frac{1}{2}$ -in. diam, 20-pitch, steel lead screw and a porous bronze nut. The nut is rubber mounted on the center line of the carriage.

For small melts only one heating coil is used on the carriage, but provision has been made for mounting two or more coils in series if required. The coil consists of four turns of compactly wound $\frac{1}{8}$ -in. copper tubing. It is slightly more than $\frac{1}{4}$ in. long and has an inner diameter of approximately $1\frac{5}{8}$ in. A flow switch in the water line cuts off the heater power in case of water failure.

For the forward motion of the carriage, the lead screw is driven through a friction clutch and reduction gears—100/1 worm and worm gear and 72/7 spur gears—by a 1/40-hp shunt-wound d-c motor. The speed of the motor is nominally 1,140 rpm, but it can be varied from about 240 to approximately 2,000 rpm by decreasing the voltage and changing the field resistance. This results in a possible variation in the rate of zone travel of from $\frac{3}{4}$ in./hr to 6 in./hr.



Automatic zone melter recently constructed at NBS. This simple and inexpensive device is used to obtain extremely high purity in semiconducting materials. Center: Water-cooled radiofrequency work coil used to melt the solid material to be purified. Coil surrounds a carbon boat which holds the bar of material. Driving motor and return motor are on right and left, respectively. Box in the foreground contains the motor controls.

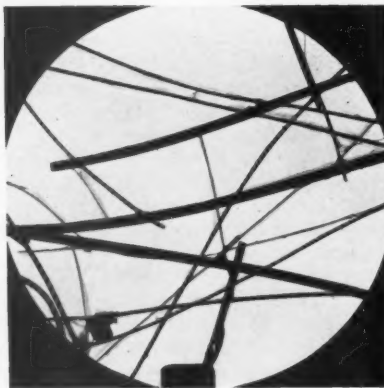
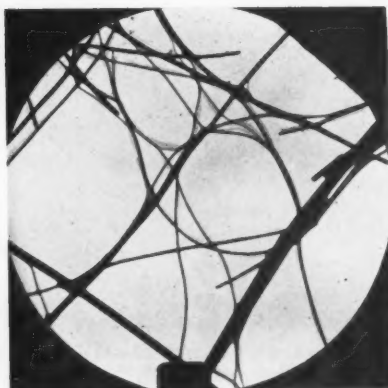
Adjustable stops on a simple push-pull rod, which actuates a toggle switch, limit the length of travel of the work coil. The stops may be set to allow a minimum travel of 1 in. or a maximum of 18 in. When the coil has reached a predetermined point, a fork on the carriage engages one of the stops and the switch is closed. This starts a $\frac{1}{10}$ -hp intermittent-duty motor which is directly coupled to one end of the lead screw. The rotation of the screw is reversed, and the carriage returns to its initial position at the rate of 75 in./min. This increased speed is sufficient to prevent the specimen from melting on the return portion of the cycle even though the heater current is not interrupted. When the carriage has reached the initial position, the fork engages the other of the two stops, causing the rod to open the switch and to stop the return motor.

A feature of the NBS device is a simple spring-load-friction clutch. This permits the slow-speed drive motor to operate continuously, even during the rapid return of the carriage, thus eliminating the need for a more complex clutch and switching arrangement. An automatic counter registers each complete cycle.

For convenience all controls are compactly arranged in a $6 \times 7 \times 10$ -in. metal cabinet. Included are the controls for the d-c motor, the transformer for the a-c motor, switches to reverse either motor, and the fuses. Input to this unit is 110 v, both alternating and direct current. The connection is made through an eight-conductor cable and a plug and socket.

Since its construction the Bureau's apparatus has been in almost constant operation and has performed very satisfactorily with a minimum of attention. It is now being used at NBS to produce a series of intermetallic compounds formed between the metal antimony and the metals indium, gallium, or aluminum.

Improved



Left: Electron micrograph of glass fibers developed by the Bureau. The high strength of the material can be seen at most intersections. A thin, gelatinous layer, which may be removed by addition of sulfuric acid, is formed on the fibers during the process. Mechanical changes in the process control, were also effective in reducing the number of fibers at the intersections. Right: Fibers at the absence of adhesion between the fiber layer is formed on the fibers. (× 3800 approx). (× 3800 approx).

Glass-Fiber Paper

RESEARCH at the National Bureau of Standards has succeeded in producing an all-glass paper eight times as strong as that first made in 1951.¹ Because of its greater strength, this paper should prove much more convenient for uses such as gas masks, chemical filters, and electrical equipment,² where the unique properties of the all-glass paper have already made it particularly valuable.

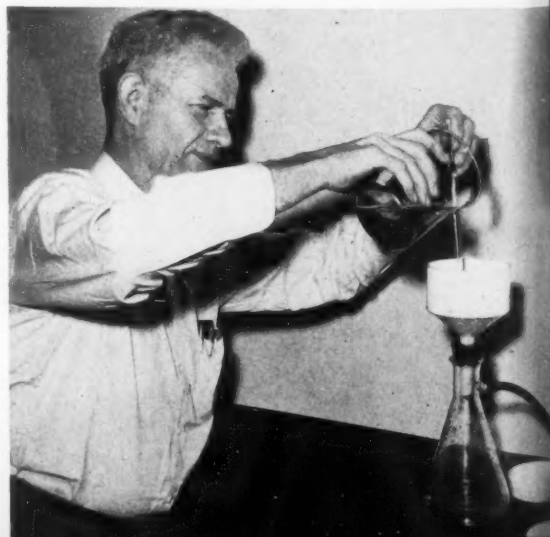
The higher strength is achieved by control of the acidity and temperature of the glass fiber suspension and by minor changes in the mechanical handling of the fibers in the paper mill. Details of the improved process were worked out in the Bureau's paper laboratory as part of a project sponsored by the Naval Research Laboratory.

Although glass fibers have been widely used for some time in textiles, such as glass curtains and filter cloths, and in plastic laminates, their use in making all-glass papers is relatively new. About 3 years ago, the Bureau, in cooperation with the Naval Research Laboratory, produced the first machine-made paper composed entirely of glass fibers without additives or binders. This paper, which resembles soft blotting paper, was found to have a number of important applications. Tests showed it to be many times more effective as an air filter than commercial filters then on the market. In gas-mask tests in a smoke-filled room, only one smoke particle in 100,000 passed through the glass-

paper filter. Another important advantage of all-glass paper is its high resistance to heat, moisture, chemicals, and microorganisms. This, in combination with excellent electrical characteristics, makes it valuable as an insulator and dielectric for special applications.

Several paper mills are now producing the all-glass

All-glass paper developed at NBS is proving very useful in filter papers as shown below. Important advantages of glass-fiber filter papers are high retention combined with high permeability to liquids and good resistance to heat, moisture, and chemicals. Because of these unique properties and the strength of all-glass paper, it should prove useful in gas masks, electrical equipment, air filters, and mine respirators. Studies are being made for possible applications as filters of hot or corrosive fluids, heat insulation, sterilizable papers for medicine and surgery, and antitarnish and anticorrosion papers.



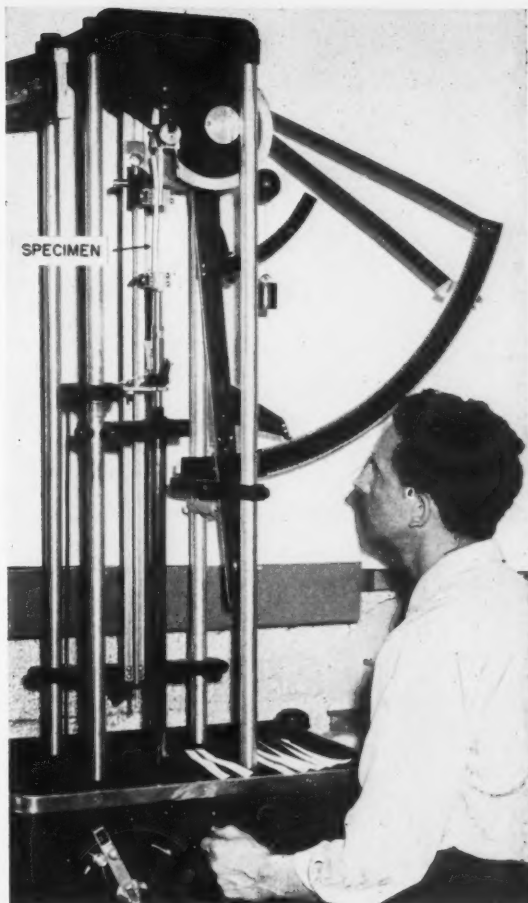
¹ See Paper from glass fibers, *NBS Tech. News Bull.* 35, 177 (Dec. 1951).

² See The electrical properties of glass-fiber paper, by T. D. Callinan, R. T. Lucas, and R. C. Bowers, *Elec., Mfg.* 48, 94 (Aug. 1951).

micrograph of the higher-strength glass-fiber paper. The Bureau has found that quantities of gelatinous binding material at most intersections of the fibers. The product, which has greater strength, was formed by the use of an acid of pH of 3.4 during the papermaking process, as well as temperature control, resulting in an improved all-glass paper. The fibers are acidified to a pH of 3.8. Note the precision of the fibers. Practically no gelatinous material is present in the fibers. Values greater (i. e., less acid) than approximately 3.8 (approx).

glass paper for military and civilian uses. The product has appeared on the market in mine respirators and gas masks and as filter disks for laboratory crucibles. It is being studied for possible use as a filter of hot or corrosive fluids, as an air filter in air conditioners, as a saturating or laminating base for plastics, and as an

useful advanced composite material, these papers, it is thought, made of glass fibers.



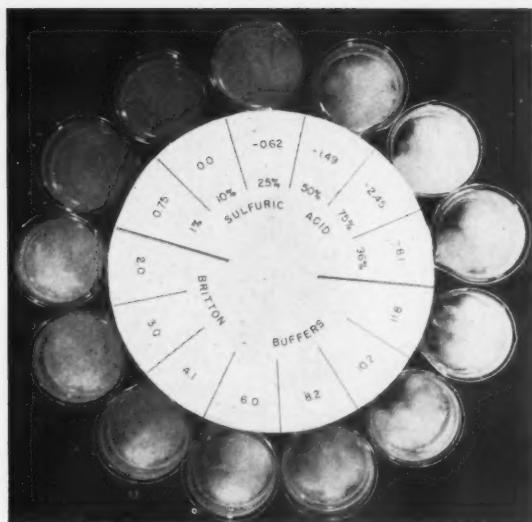
electrical insulator in coil windings, condenser and transformer cores, and battery separators. Other possible applications include heat insulation where a thin material is required, sterilizable papers for medicine and surgery, and antitarnish and anticorrosion papers.

However, for all these uses, the low tensile strength of the all-glass paper—originally 30 to 40 lb/in.²—has been a disadvantage, requiring extra care in production, storage, and handling. The improvements made in the process by NBS increase the tensile strength to more than 300 lb/in.² and should thus make the

Measurements at the Bureau show the tensile strength of the improved glass fiber paper to be more than 300 lb/in.² The strip of all-glass paper under test is suspended between two jaws at upper left. As the lower jaw is brought downward, the tension transmitted through the specimen to the upper jaw causes the pendulum at right to swing out. The tension at failure is indicated on the curved scale. Largely through control of the acidity and temperature of the glass-fiber suspension, the Bureau is now making glass-fiber paper eight times as strong as that first produced in 1951.



Above: The air-resistance of the all-glass paper, being measured here, is an important characteristic in air- and gas-filter applications.



Experimental demonstration shows graphically the effect of acid and alkali on the dispersion of glass fibers. Each beaker in the circle contains glass fibers in suspension at the indicated pH. The fibers are well dispersed between pH 2 and 4. From pH 2 down to -1, a gel is formed. Above pH 4 the fibers are clumped together, and below -1 in the acid range clumping occurs again. The fibers are in the best condition for paper making between pH 3 and 4.

glass-fiber paper considerably more practical for commercial manufacture and use.

Because the properties of glass fibers are so different from those of the cellulose fibers ordinarily used in papermaking, considerable change has been necessary in applying the usual papermaking techniques to the manufacture of glass-fiber paper. For example, in the manufacture of ordinary paper, vegetable fibers are processed with water in a "beater", which bruises the fibers and forms minute fibrillae. Mechanical entanglement of the fibrillae aids in bonding the fibers together. In addition, prolonged beating is thought to increase the adsorption of water on the fibers, which enhances fiber-to-fiber bending when the fibers of the paper are dried in close contact.

With glass fibers, on the other hand, no fibrillation takes place, and no significant hydration ordinarily occurs. Because bruising breaks the fibers and tends to weaken the paper, the beater is adjusted to eliminate most of the pressure on the fibers and is used merely for suspension and circulation of the fibers.

In the glass papermaking process as improved at the Bureau, beating is conducted at a temperature of 85° F, and the pH of the glass-water mixture is adjusted to 3.5 or less by adding sulfuric acid. Under these conditions, the fiber bundles open up and are dispersed more quickly, less fiber breakage occurs, and the resultant paper is stronger.

Mechanical changes have been made in the equipment to eliminate strings or lumps in the finished paper. Because glass fibers in the stock flow system of a paper mill tend to accumulate on any projection or rough place, sharp angles were eliminated from the piping. A horizontal stock chest with agitators moving in a vertical plane was also installed so that the fibers would fall back into the liquid instead of accumulating in strings as they do on horizontal agitators.

When the fiber suspension was brought to a pH of

3.0 as it entered the jordan, it was found possible to pass it through the jordan refiner of the paper mill without damage to the fibers, a step that had hitherto been impossible. Treatment in the jordan also helped to break down strings and knots, resulting in a much improved formation in the finished sheet.

Previously it was necessary to maintain a fairly high moisture content in the all-glass paper in order to carry it onto the reel of the paper mill, for the glass paper has a higher tensile strength when wet than when dry. The additional strength was sufficient to eliminate breakage between the dryers and the reel. However, glass papers made by the Bureau's improved process have enough strength that they can be dried to the same extent as cellulose papers and still be carried onto the reel without breaking.

Photomicrographs made at the Bureau show the effect of a lower (more acid) pH in binding the fibers together to give higher strength. Ordinarily acid reacts so slowly with glass as to have negligible effect. However, the very fine glass fibers expose a tremendous surface to the acid, which starts to dissolve the soda and lime in the glass, leaving on its surface a thin gelatinous layer, rich in silica. When the water drains from the fiber suspension on the wire of the papermaking machine and the fibers are pressed together, this gelatinous layer acts as an adhesive to bond the fibers together in the paper. The pH value must be below 4 to obtain this effect, and the tensile strength increases as the pH decreases in the range studied (down to 2.9). Ionizable acid is drained off during the formation of the sheet, so that the pH of the finished paper is effectively neutral—from 7.0 to 7.4.

The use of acid also causes rapid dispersal of the fibers in the beater. This may be due in part to an ionic electrical phenomenon resulting from the initiation of the chemical reaction between the acid and the glass. It is known that negative electrical charges appear on the surface of the glass, and the mutual repulsion of the like-charged surfaces is probably responsible for the quick separation of the fibers.

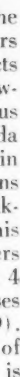
A temperature of 85° F in the beater likewise aids in promoting dispersion of the glass fibers. The decreased viscosity and interfacial tension of the heated water apparently cause it to wet and penetrate the fiber bundles more readily.

For further technical details, see Effects of mechanical preparation and pH on the strength of glass-fiber paper, by Martin J. O'Leary, Robert B. Hobbs, J. K. Missimer, and James J. Erving, *Tappi* 37, 46 (1954).

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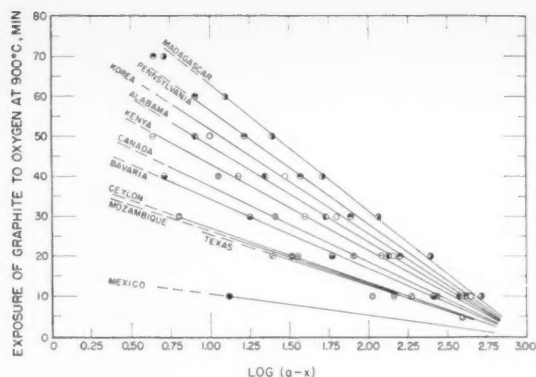
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No. 16 sieve and remaining on the No. 20 sieve was selected for this group.

Oxidation rate, amount of volatile matter, and graphitic content of the samples were determined with a carbon train apparatus. The equipment consisted essentially of three parts: (1) Absorption tubes for purifying the gas, (2) a multiple-unit electric-tube furnace, and (3) absorption tubes for the products of combustion. When a sample was to be processed, approximately 0.1 g of the graphite was placed in a combustion boat and heated to 110° C to remove the moisture. It was then inserted into the tube furnace which was preheated to 900° C. To remove volatile matter, the graphite sample was heated for successive 15-minute periods in an oxygen-free nitrogen atmosphere. After each heating period, it was cooled and weighed. The process was continued until a constant weight was attained.

The oxidation rate was found by measuring the rate of evolution of carbon dioxide from a dry volatile-free graphite sample. The sample was heated in the tube furnace at 900° C in an oxygen stream. The carbon dioxide resulting from the oxidation was absorbed in tubes containing both ascarite and magnesium perchlorate. The tubes were weighed at intervals during the run until no further gain in weight was indicated. The weight of the carbon dioxide was multiplied by the ratio between the weights of carbon and carbon

oxide to find the weight of the carbon alone, and the percentage of graphitic carbon was then found by dividing the total weight of the carbon by the weight of the dry volatile-free graphite sample. The residue from the oxidation test is considered ash. All samples had been refined to contain at least 85 percent graphite.

Average flake thickness of the samples was determined by measuring individually 75 to 100 flakes in a machinist's micrometer. Since surface area of the particle is related to rate of oxidation, it was obtained using the nitrogen sorption method.

From the analyses made in this investigation, it was found that the oxidation rate of graphite generally increases as particle size decreases. This change in oxidation rate is to be expected since the rate of reaction of a solid with a gas depends on the surface of the solid exposed to the gas at any given instant. For the 11 graphites from foreign and domestic sources, the best correlation noted was that of the oxidation rates with surface areas obtained by the nitrogen sorption method. It was also discovered that the Alabama and Pennsylvania samples had oxidation rates that were not greatly different from those of the corresponding particle sizes of samples representing the graphites imported in large quantities from Madagascar. Of the 10 samples from 10 different Madagascar deposits, 4 different distinct oxidation rates were noted. As a final result of this study, a set of numerical constants was established for the oxidation rates of natural graphites. These constants should prove useful in the future selection of particular graphites and particle sizes for individual applications.

For further technical details, see Oxidation studies of some natural graphites, by R. A. Heindl and N. F. Mohler, *J. Ceramic Soc.* (March 1955).

TABLE 1. Oxidation rates for fractions of graphites from different deposits

Source of graphite	Moisture	Volatile matter at 900° C	Oxidation rate (min ⁻¹) of fractions passing and remaining on sieves No. ^a								
			8-16	16-20	20-30	30-40	40-50	50-60	60-80	80-100	Through 100
Madagascar	^b 0.45	^c 2.18	0.037	0.043	0.070	0.079	0.076	0.087	0.146	0.174	0.247
Pennsylvania (U. S. A.)	^b .36	^c 1.72	.045	.060	.057	.079	.080	.108	.131	.222	.248
Korea	^c .48	^c 1.56091
Alabama (U. S. A.)	^b .50	^c 2.39	.049	.060	.080	.102	.101	.100	.107	.119	.247
Kenya	^c .29	^c 2.45107
Canada	^c .09	^c 1.13112
Bavaria	^c .38	^c 1.03
Ceylon	^c .10	^c 2.75	^d 0.130 (0.129)
Mozambique	^c .39	^c 1.57	^d .157 (0.165)
Texas (U. S. A.)	^c .28	^c 1.14	^d .169 (0.173)
Mexico	^c .36	^c 2.88	^d .177 (0.184)
			^d .463 (0.461)

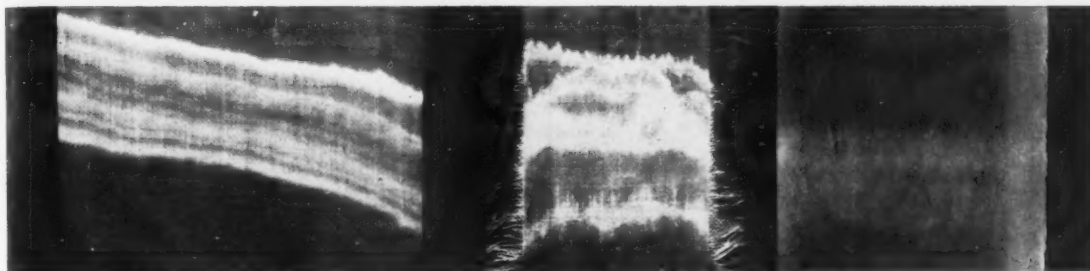
^a U. S. Standard Series.

^b Average of 18 determinations.

^c Average of 2 determinations.

^d Values in parentheses are duplicate determinations.

Brown-Line Effect on Fibrous Materials



"Brown-line" effect as shown by ultraviolet light. *Left to right:* Cotton cloth after immersion in water, cotton cloth after experiment with chloroform, and nylon cloth after experiment with chloroform. The water-soluble brown line formed at the boundary between wet and dry areas on fibrous materials fluoresces markedly in ultraviolet light.

THE BUREAU has extended its previous research on moisture effects in cotton textiles to a more general investigation of the effects of both water and organic liquids on fibrous materials. The boundaries between wet and dry areas on cotton, nylon, acetate, and quartz fibers have been found to be regions of exceptional chemical activity in a study conducted by R. Schaffer, W. D. Appel, and F. H. Forziati of the Bureau's textile laboratory. Results of this work indicate that either the fibers or the evaporating liquid at the boundary undergo oxidative changes in a few hours or days, even at room temperature. In view of the frequency with which wet-dry interfaces occur during the processing and use of textiles, papers, and other fibrous materials, it appears that the reactions studied by the Bureau may be of wide interest.

When water evaporates from cotton cloth, a brown line is often observed at the boundary between the wet and dry areas. In 1952 the Bureau investigated this effect in a series of experiments¹ in which one end of a strip of cotton cloth was kept immersed in water in the presence of air at room temperature. A water-soluble brown line which fluoresced in ultraviolet light was formed at the wet-dry interface. When the brown material was extracted from the cloth, it was found that the cloth had been converted to oxycellulose of an acidic, mildly reducing type, with consequent weakening of the material.

¹ See Some observations on the evaporation of water from cellulose, by Herman Bogaty, Kenneth S. Campbell, and William D. Appel, *Textile Research J.* **22**, 75 (1952).

In the present investigation, similar experiments were carried out using cotton cloth with benzene, xylene, chloroform, and *n*-pentane; nylon cloth with *n*-pentane and with water; acetate cloth with water; and quartz-fiber paper with *n*-pentane. In each of these experiments, fluorescence followed by browning developed at the boundary between wet and dry areas within a day or so.

To determine the importance of oxygen to the reaction, experiments using nylon cloth and quartz-fiber paper with *n*-pentane were carried out in an atmosphere of nitrogen instead of air. The "brown-line" reaction did not occur. Negative results were also obtained in experiments carried out in air but so arranged that *n*-pentane rose by capillarity to the top of specimens of cotton and nylon cloths. Thus, the presence of oxygen and of contiguous wet and dry areas appears to be essential to the reaction.

The brown-line products from the experiments with cotton and organic liquids, unlike those obtained with cotton and water, are soluble in organic liquids but insoluble in water. That these products are derived from the organic liquids instead of the cellulose is suggested by the failure of the cloth to show the characteristic reactions of oxidized cellulose. As quartz is not subject to oxidation, there can be little doubt that the brown line obtained with quartz-fiber paper and *n*-pentane is derived from the *n*-pentane.

For further technical details, see Reactions at wet-dry interfaces on fibrous materials, by Robert Schaffer, William D. Appel, and Florence H. Forziati, *J. Research NBS* **54**, 103 (1955) RP2570.

Publications of the National Bureau of Standards

Journal of Research of the National Bureau of Standards, volume **54**, number 5, May 1955 (RP2586 to RP2592 incl.). Annual subscription \$4.00.

Technical News Bulletin, volume **39**, number 5, May 1955. 10 cents. Annual subscription \$1.00.

CRPL-129. Basic Radio Propagation Predictions for August 1955. Three months in advance. Issued May 1955. 10 cents. Annual subscription \$1.00.

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Journal of Research, volume **54**, number 5, May 1955. Single copies of the *Journal* vary in price. Single copies of *Research Papers* appearing in the *Journal* are not available for sale. The Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., will reprint 100 or more copies of a *Research Paper*. Request for the purchase price should be mailed promptly to that office.

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NATIONAL BUREAU OF STANDARDS

A. V. ASTIN, *Director*

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- Electrolytic coatings on magnesium base alloys from alkaline chromate solutions. F. Ogburn, H. I. Salmon, and M. L. Kronenberg. *Plating* (445 Broad St., Newark 2, N. J.) **42**, 271 (1955).

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